Dissolved Manganese in Drinking Water on the Gulf Islands: Occurrence and Toxicity

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1 Introduction

Groundwater is the primary source of drinking water for most residents on the Gulf Islands in British Columbia, Canada. Groundwater is primarily derived from drilled wells completed in bedrock; however, shallow dug wells completed in surficial sediments provide potable water on some islands. The bedrock consists primarily of rocks of sedimentary origin (interlayered sandstone- to mudstone-dominant formations) that make up the Upper Cretaceous age Nanaimo Group.

Chemical results for samples of drinking water collected from domestic and community wells on Hornby and Saturna Island during two island-wide research projects revealed high concentrations of dissolved manganese. At the time of sampling, 31 sites on Hornby Island and 38 sites on Saturna Island had concentrations greater than or equal to the level outlined in the Canadian Drinking Water Guidelines. Several residents on Hornby Island, who had previously had their own wells tested for various dissolved metals and were alerted to the high levels of manganese, indicated concern about the human health effects related to the high concentrations of manganese in their drinking water. Further, there was some speculation on the part of residents that high manganese concentrations on Hornby Island may be related to a local landfill.

1.1 Scope of Work

This report has been prepared for the Islands Trust and the BC Ministry of Environment, Lands and Parks as a gratuitous supplement to the reports on the groundwater geochemistry on Hornby and Saturna Islands. The focus of the report is dissolved manganese in drinking water (primarily groundwater) on two Gulf Islands. The report contains the following:

- A discussion of manganese toxicology and the human health effects with respect to exposure to manganese and the ingestion of water with high concentrations of manganese;
- Maps showing the point sample values and the spatial distribution of dissolved manganese in waters collected on Saturna and Hornby Islands.
- A discussion of the possible correlation between geology, other dissolved species and the distribution of manganese.

Manganese concentration data are contained in undergraduate theses prepared for Saturna (Suchy, 1998) and Hornby Island (Matsuo, 2000), respectively.

Manganese toxicity was researched by an undergraduate student, Krista Pelude, at Simon Fraser University in partial fulfillment of course requirements. Toxicity information for both non-dissolved and dissolved manganese has been summarized from published information and does not reflect the opinions of the authors. This work also represents

preliminary findings of ongoing research into the origin of dissolved chemical constituents in groundwaters on the Gulf Islands, and may be modified as new data are obtained or as new interpretations are developed.

1.2 Canadian Drinking Water Guidelines

The current Canadian Drinking Water Quality guidelines list maximum acceptable concentrations, interim maximum acceptable concentrations and aesthetic objectives for chemical and physical parameters in drinking water. Manganese has been assigned an aesthetic objective of less than or equal to 0.05 mg/L (1999, Federal-Provincial Subcommittee on Drinking Water).

Manganese was assigned an aesthetic objective because it is not considered a toxin in drinking water. The objective was set because manganese stains plumbing fixtures and laundry, and produces undesirable tastes in beverages at concentrations greater than 0.15 mg/L. It can also lead to the accumulation of microbial growths on distribution systems. Negative aesthetic effects can occur even at concentrations less than 0.05 mg/L. Manganese can also form coatings on piping that might slough off as black precipitate, and can potentially clog well pumps and screens.

2 Manganese Toxicology

2.1 Physical and Chemical Properties

Manganese is a trace element, which was discovered in 1774 by Gahn. Its atomic symbol is Mn. Manganese is classified as a transition element with an atomic number of 25 and an atomic weight of 54.938. The melting and boiling points of Mn are 1224°C and 1962°C, respectively. Solid manganese has a density of 7.43 g/cm^3 and is considered insoluble in water (Zumdahl, 1995) although it is common for manganese to occur in generally small amounts in natural waters. Oxidation states can range from –3 to +4. +6, and +7, with +2 being the most stable and common in water. Mn^{2+} Mn^{4+} and Mn^{7+} are the most environmentally important.

There are a number of manganese compounds of industrial importance including manganese chloride ($MnCl_2$), tri-manganese tetroxide (Mn_3O_4), manganese dioxide (MnO_2) and potassium permanganate ($KMnO_4$). $MnCl_2$ has a melting point of 650°C, a boiling point of 1190°C, a density of 2.97 g/cm^3 and a water solubility of 723 g/L. Mn_3O_4 has a melting point of 1564°C, a density is 4.86 g/cm^3 and is insoluble in water. MnO_2 has a density of 5.03 g/cm^3. $KMnO_4$ has a density of 2.70 g/cm^3 and has a water solubility of 63.8 g/L (WHO, 1996).

2.2 Exposure and Environmental Levels

Manganese is a naturally occurring substance in the environment. It is an abundant mineral in the earth's crust and is present in over one hundred common salts and mineral complexes that are widely distributed in rock, soils and on the floors of lakes and oceans. Manganese is most often present as an oxide, but can occur as a carbonate or silicate. Manganese can also be found in both plants and animals and is, therefore, present in foods.

The concentration of manganese is approximately 5ng/m^3 in the ambient air of non-industrialized areas. Concentrations can increase to approximately 33ng/m^3 in industrialized areas, and in areas close to manganese-related industry, air levels can reach 0.13 ug/m^3 or greater (WHO, 1996).

Manganese concentrations in surface water bodies (i.e., lakes and rivers) around the world range from 0.001 to 0.06 mg/L. If higher levels are found in aerobic waters, this is usually associated with industrial pollution because aerobic conditions tend to favour precipitation of manganese as oxides. In contrast, high concentrations of manganese have been measured in anaerobic water (both surface water and groundwater). Manganese concentrations as high as 1.3 mg/L occur in neutral water and concentrations as high as 0.6 mg/L in acidic water (WHO, 1996). Manganese is more prevalent in groundwater supplies than in surface water supplies due to reducing conditions underground (WHO, 1996).

Manganese is also present in food. Manganese concentrations ranging from 0.02 to 0.5 mg/kg were detected in dairy products. Meats, fish and eggs ranged in concentration from 0.1 to 4 mg/kg, while vegetables had concentrations as high as 0.41 to 6.61 mg/kg. In grains and cereals, concentrations ranged from 0.41 to 4 mg/kg, while in nuts concentrations ranged from 18 to 47 mg/kg. Therefore, the greatest exposure to manganese is usually from food.

Adults usually consume 2 to 20 mg/day of manganese; 2 to 5 mg/day is the average daily manganese nutrient requirement for normal physiological function. No adverse effects were observed in humans after daily intakes of 2.0 to 7.0 mg/day in food, 0 to 1.0 mg/day in water, and 0 to 0.029 mg/day in air (SHO, 1996).

Exposure to high levels of manganese is most likely to take place in industry, where manganese metal is produced from manganese ores, or where manganese compounds are used to make steel or other products. Manganese dioxide and other manganese compounds are also used in products such as batteries, glass and fireworks. Potassium permanganate is used as an oxidant in cleaning, bleaching and disinfection processes.

Exposure in industry will occur in most cases through dust inhalation. Exposure to manganese dust can also take place in areas surrounding these industries as well as near coal or oil burning factories or major highways because combustion of fossil fuels releases manganese to the air. Contamination of water sources can also result in elevated levels of dissolved manganese (ASTDR, 1992).

2.3 Chemical Relations

Manganese often occurs together with iron. It resembles iron in its chemical occurrence in groundwater, but is less abundant. Dissolved manganese concentrations in ground and surface water can reach several milligrams per litre under poor oxygen conditions. This often occurs in deep wells. If exposed to oxygen, manganese can form insoluble oxides that may result in the formation of deposits and colour alteration. Soluble manganese can become insoluble through the following chemical reaction:

$$2Mn(HCO_3) + O_2 + 2H_2O \rightarrow 2Mn(OH)\downarrow + 4CO_2\uparrow$$

Therefore, when soluble manganese bicarbonate dissolved in water is exposed to higher concentrations of oxygen, oxidation of the compound takes place. A new insoluble manganese oxide is formed and precipitates out of solution. Carbon dioxide is lost from the system as gas. In other words, it is expected that elevated manganese concentrations will exist in anaerobic conditions. The manganese hydroxide precipitate has the consistency of gel and may over time develop into black scale deposits.

2.4 Environmental Fate

Elemental and inorganic forms of manganese may be present in the atmosphere as suspended particles. Both dissolved and suspended forms of manganese occur in surface waters. In situations where groundwater is anaerobic, elevated levels of dissolved manganese may be present. At pH 4-7, the divalent form of manganese (Mn^{2+}) predominates in water, but more highly oxidized forms may occur at higher pH values or result from microbial oxidation. Depending on organic content and cation exchange capacity of the soil, manganese can be absorbed onto soil. It can bioaccumulate in lower organisms but not higher organisms, so that biomagnification in food chains is not significant (WHO, 1996).

2.5 Uptake Routes

In humans, the main uptake routes are through the respiratory and gastrointestinal tracts. Cutaneous absorption of inorganic manganese may occur in small amounts, whereas, organically bound manganese may be absorbed through the skin (Federal-Provincial Subcommittee on Drinking Water. 1999).

Inhalation of manganese dust results in dust particles being trapped in the lungs, and subsequently, enter the circulatory system. Those particles that are not dissolved in the blood will be removed from the lungs in the form of mucus into the throat, where the mucus will be swallowed into the stomach (Federal-Provincial Subcommittee on Drinking Water, 1999).

Absorption of manganese through the small intestine takes place by a high affinity, low capacity active transport mechanism. Approximately 3 to 8% of an ingested dose is absorbed. With increasing age the absorption of manganese decreases, for example, in a young infant, absorption of manganese is very high, approaching 99% at birth, and with age, adsorption gradually decreases to approximately 5.5% in an adult.

A large number of dietary factors influence the absorption of manganese in humans. Manganese bioavailability can be enhanced when taken in at low concentrations by the addition of ascorbic acid and meat containing diets. It can also be inhibited by some dietary fiber sources. Several metal ions, in particular ion, magnesium and calcium, are known to decrease the absorption and retention of manganese. There is evidence that uptake is higher from soft drinking water than from hard drinking water (Federal-Provincial Subcommittee on Drinking Water, 1999). As many groundwaters on the Gulf Islands are relatively soft (Allen and Suchy, in press), manganese uptake may be enhanced.

The body on the whole is able to regulate the uptake and storage of manganese. The total amount of manganese usually remains constant, even when exposure rates are higher or lower than usual except in cases of extreme deficiency or uptake. In cases of extreme uptake the body may not be able to adjust and health effects may occur.

2.6 Metabolism and Storage Sites

Manganese is present in all tissues of the body. In an adult human the total body burden of manganese is between 10 and 20 mg. The highest amount is found in the bones at approximately 25% of the body burden. Most of the manganese seems to be deposited in the inorganic portion of the bone, which acts as a buffer. Accumulation of manganese also occurs in tissues that are rich in mitochondria and endoplasmic reticulum. The liver, skeletal muscle, connective tissue and the intestine are the principal sites of accumulation after the skeleton. The tissues that accumulate the most manganese with respect to concentration (μg Mn/g tissue) are the testes, liver, pancreas and kidneys. Manganese accumulates preferentially in certain regions of the brain in infants and can also be detected in the hair (Klimis, 1994).

Manganese may undergo changes in oxidation state within the human body. It has many roles in the body; it is a constituent of the enzymes pyruvate carboxylase and superoxide dismutase, and is required as a cofactor in a number of enzyme systems. It plays a role in flavoprotein function and the synthesis of sulfated mucopolysaccharides, cholesterol and haemoglobin (WHO, 1996).

2.7 Excretion

The main homeostatic mechanism for manganese is the regulation of manganese excretion. There is also some evidence that regulation of absorption can also aid in homeostasis. Excretion of endogenous manganese is via the liver in bile for eventual elimination in the faeces. Pancreatic and other intestinal secretions increase when the biliary system is overloaded. Re-absorption of manganese can occur but in small amounts, and may be dependant on the amount of calcium in the faeces. This makes it difficult to quantify biliary excretion routes, as reabsorption can occur. Excretion can also occur in the urine. Variations in dietary manganese have little effect on the amount of manganese excreted in the urine (Klimis, 1994).

There are relatively few data describing the rate of elimination of manganese from humans. In a recent study involving 14 subjects, it was shown that two sequential processes with average biological half-lives of 13 and 34 days eliminated orally administered manganese. Both the rate of excretion and the amount of manganese eliminated are influenced by a number of factors, including manganese intake, the iron status in the body, the influence of other dietary components and in the differences in the genetic make-up of the individual (WHO, 1996).

2.8 Deficiency and Toxicity

Manganese consumption is an important part of a human's daily diet. Approximately 2 to 5 mg/day is enough is enough to meet daily dietary needs. To date there are no reports of human illness due to not enough consumption of manganese.

In cases of high manganese uptake, serious illness can incur. A disease known as manganism has been experienced by manganese miners and steel workers who are exposed to high levels of manganese dust in the air over many moths or years. Symptoms include mental and emotional disturbances, and body movements may become slow and clumsy. Some symptoms can be reduced by medical treatment, but manganese injures a part of the brain that controls body movements and this is permanent. The inhalation of dust can also result in lung irritation, which causes difficulty in breathing and may increase the chances of lung infection such as pneumonia. Men exposed to high levels of dust in the air may also become impotent (Federal-Provincial Subcommittee on Drinking Water, 1999).

3 Health Effects of High Manganese Concentration in Drinking Water

While there is a significant amount of information of the health effects of direct exposure to manganese, the amount of information on dissolved manganese is limited. This section summarizes some of the documented health effects of high manganese concentrations in drinking water.

There is some controversy as to whether neurological effects exhibited with inhalation exposures will also occur with oral exposures. It is not certain that manganese ingested in large amounts will have the same effect as the inhalation of manganese dust. To date there have been few studies done on this subject and no convincing evidence of toxicity in humans associated with the consumption of manganese in drinking water.

In 1941, a reported outbreak of manganese toxicity occurred in Hiratsuka, Japan. The outbreak affected 16 individuals; five cases were severe, two were moderate and nine were mild. Symptoms included lethargy, increased muscle tonus, tremors and psychiatric disturbances. Two of the severe cases died and one case committed suicide due to melancholy. The outbreak occurred due to the consumption of water from three wells that were contaminated with manganese. The manganese was derived from 400 dry-cell batteries buried near the drinking wells. The exposure occurred over 2 to 3 months, which is a relatively short time period considering the exposure time required for symptoms related to dust inhalation. The first measurement of the well water took place 7 weeks after the first illness. The measured concentration of manganese was 14 mg/L and it was found through subsequent sampling that the concentration decreased rapidly. It can be assumed that the initial manganese concentrations in the well water could have been considerably higher, some suggesting 28 mg/L. The concentrations of other metals such as zinc were also in excess and it was never unequivocally established that manganese was the sole reason for the outbreak (Klimis-Tavantzis, 1994).

An epidemiological study was conducted in Greece to investigate the possible neurological effects in the elderly with respect to high manganese concentrations in drinking water (Kondakis, 1989). Three areas in the same region of Peloponnesos, Greece, which had varying concentrations of manganese in the drinking water were studied. Manganese concentrations in the control area ranged from 3.6 to 14.6 μg/L; 81.6 to 252.6 μg/L and 1800 to 2300 μg/L in the two study areas, respectively. The authors concluded that progressive increases of Mn concentration of drinking water are associated with progressively higher prevalence of neurological signs of chronic manganese poisoning and Mn concentration in hair of the elderly. This report would suggest that chronic consumption of water containing 2 mg/L of Mn or more may represent a health hazard. It must be noted that Mn intake resulting from dietary habits and dust inhalation were ignored (Kondakis, 1989). It is still not clear what constitutes a safe level of manganese in drinking water.

A study conducted in northern Germany, also tried to determine the relationship between long-term exposures to manganese in rural well water with neurological effects

in the elderly (Vierregge, 1995). Manganese burden from rural well water was studied cross-sectionally between two groups of people with common statistical characteristics. The groups were separated on the basis of manganese concentration in the well water; the first group having an average well concentration of 0.3 mg/L and the second group having a well concentration of 0.05 mg/L. It was found that no significant difference in any neurological measure was found between the groups. Therefore, it was concluded that exposure to manganese in drinking water does not seem to be a risk factor for manganism disease (Vierregge, 1995).

4 Manganese Concentrations on the Gulf Islands

Water sampling was conducted at 127 sites on Hornby Island and 95 sites on Saturna Island. Manganese concentrations ranged from 0.001 mg/L to 0.97 mg/L on Saturna Island (Figure 1) and from 0.001 mg/L to 1.05 mg/L on Hornby Island (Figure 2). At the time of sampling, 31 sites on Hornby Island and 38 sites on Saturna Island had concentrations greater than or equal to the 0.05 mg/l limit provided in the Canadian Drinking Water Guidelines. With approximately one third of those waters samples testing above the drinking water limits on each island, it is clear that manganese occurs at somewhat anomalous concentrations on the Gulf Islands. The objectives of this section are to describe the spatial distribution of dissolved manganese, to comment on possible correlation with other dissolved species in water, and to determine if the source is geological or anthropogenic.

From chemical data provided for Saturna and Hornby Island, manganese concentration distribution maps were created for the islands. The data were imported into a computer contouring package (Surfer) and maps showing the spatial distribution of manganese were produced. It is important to note that the grid area for each map extends beyond the island outlines. This occurs because the contouring package extrapolates data beyond the furthest data point. Consequently, all values beyond the island outline limit should be disregarded.

These concentration maps are shown in Figures 3a and b (Saturna Island) and Figures 4a and b (Hornby Island). Figures 3a and 4a show the concentration of manganese expressed as a logarithm (i.e., 0.01 mg/l = 10^{-2} mg/l, therefore log 10^{-2} = -2). The logarithm maps permit the wide range of values (spanning over one order of magnitude) to be contoured more effectively (eliminates the bulls-eye effect associated with extreme values). Figures 3b and 4b show the concentrations of manganese in mg/l and tend to accentuate the samples with extreme values.

4.1 Manganese Distribution on Saturna Island

High concentrations of dissolved manganese are found in four areas on Saturna Island (Figure 3a and b). The highest concentration was measured from a surface water sample collected from Money Lake, located north of Mt. Fisher and Mt. Warburton in the center of the island. Money Lake provides drinking water to many residents on Saturna. Other areas with high concentrations include East Point peninsula located at the northeastern tip of the island, Winter Cove at the northwestern tip of the island, and Lyall Harbour at the northwest end of the center of the island. Saturna Beach at the southern side of the island, also has elevated manganese levels. Samples from these areas are all groundwater.

The anomalous high concentration of manganese in Money Lake is curious and difficult to attribute to any particular factor. Money Lake is located in Northumberland Formation rocks (mudstone-dominant) and likely receives surface water runoff (and possibly some groundwater discharge) from the elevated areas around Mt. Fisher and Mt. Warburton

(Figure 5 shows general recharge areas for Saturna Island based on the chemical evolution of groundwater on the island).

The other areas of elevated manganese concentration are not associated with any particular geological formation (Figure 5), but appear to be concentrated in wells in low-lying areas possibly corresponding to discharge areas. It is important to note that most samples were collected from coastal well, however, and this may bias the interpretation. From a geological perspective, high concentrations are found in groundwaters in the Geoffrey (sandstone), Protection (sandstone), and possibly the Northumberland Formation (Winter Cove area).

4.2 Hornby Island

High concentrations of dissolved manganese are found in several areas on Hornby Island (Figures 4a and b). Unlike Saturna Island where development is focused along the coast, samples from Hornby Island are well distributed across the island (both central and coastal areas).

There does not appear to be any spatial correlation between areas of elevated manganese and the location of recharge and discharge areas (Figure 7) or the geology (Figure 8).

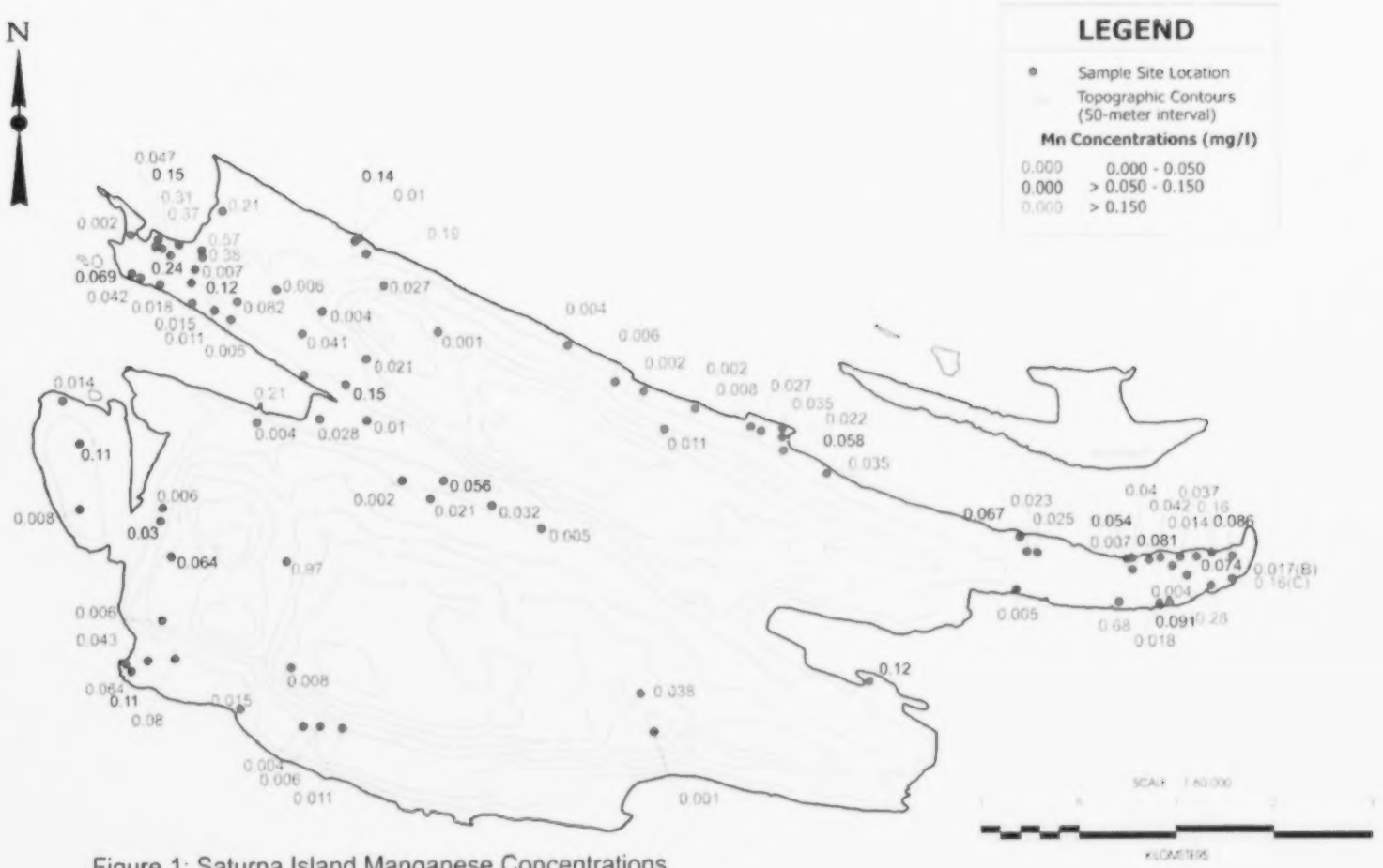


Figure 1: Saturna Island Manganese Concentrations

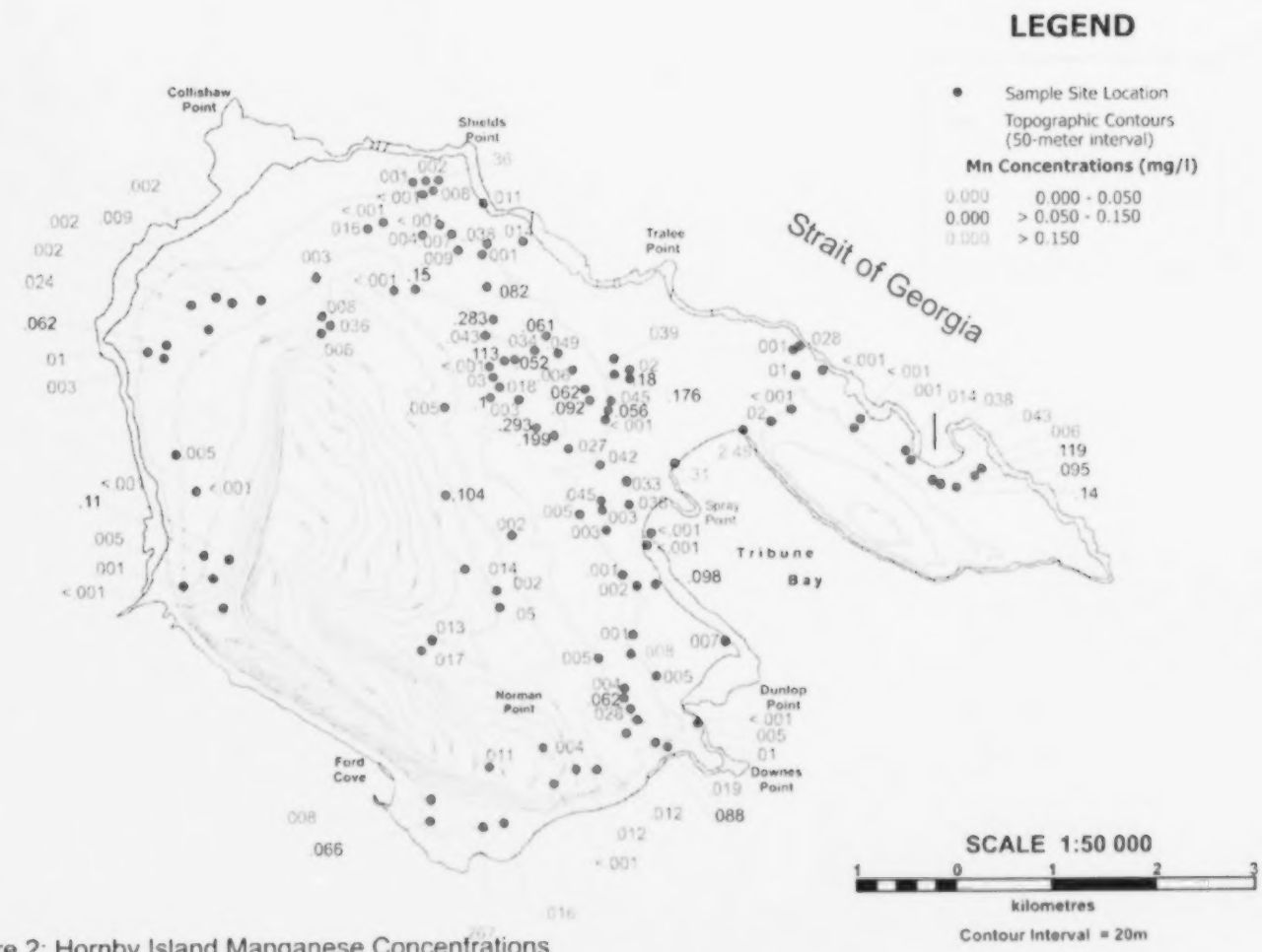


Figure 2: Hornby Island Manganese Concentrations

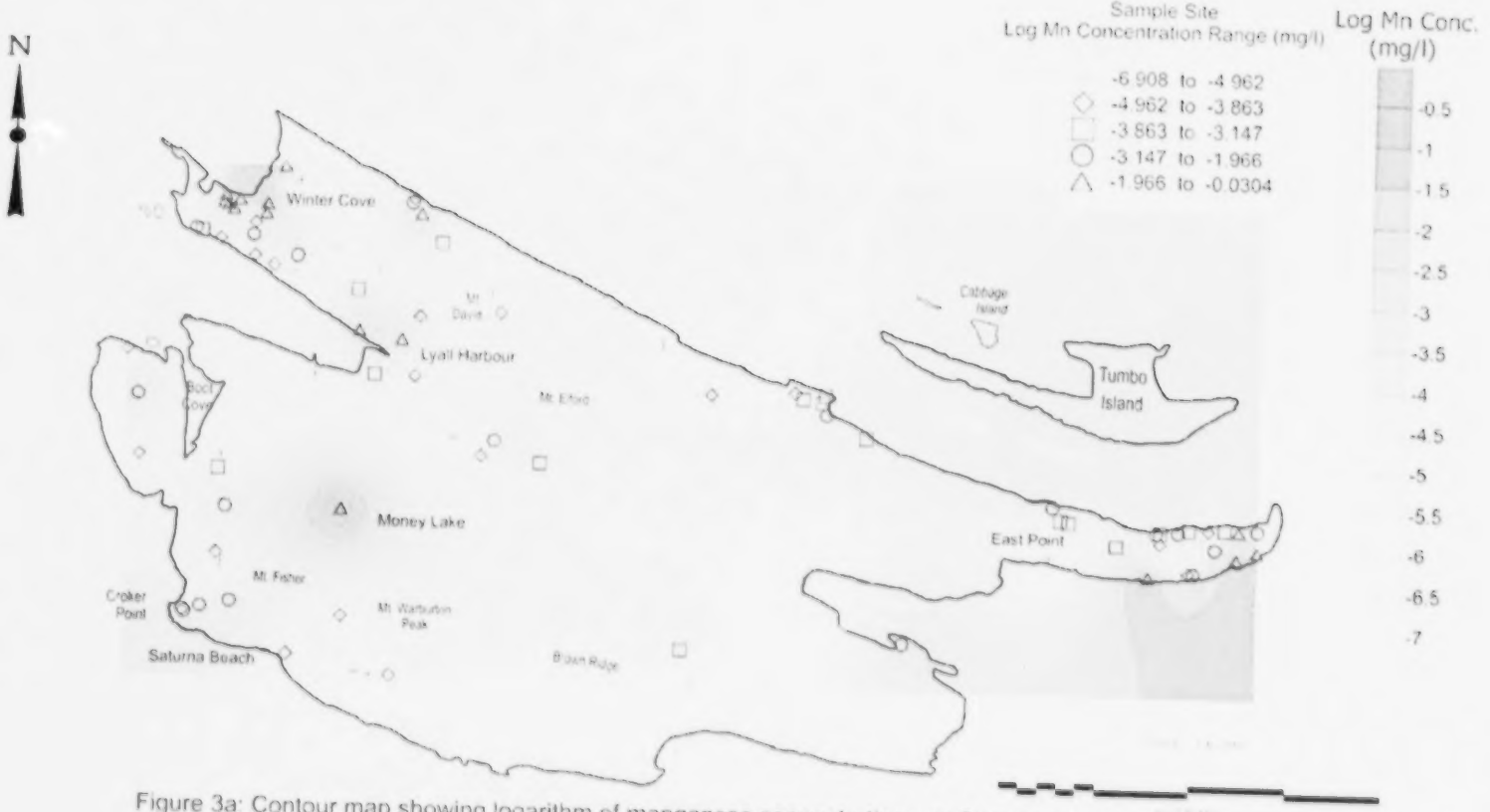


Figure 3a: Contour map showing logarithm of manganese concentrations on Saturna Island

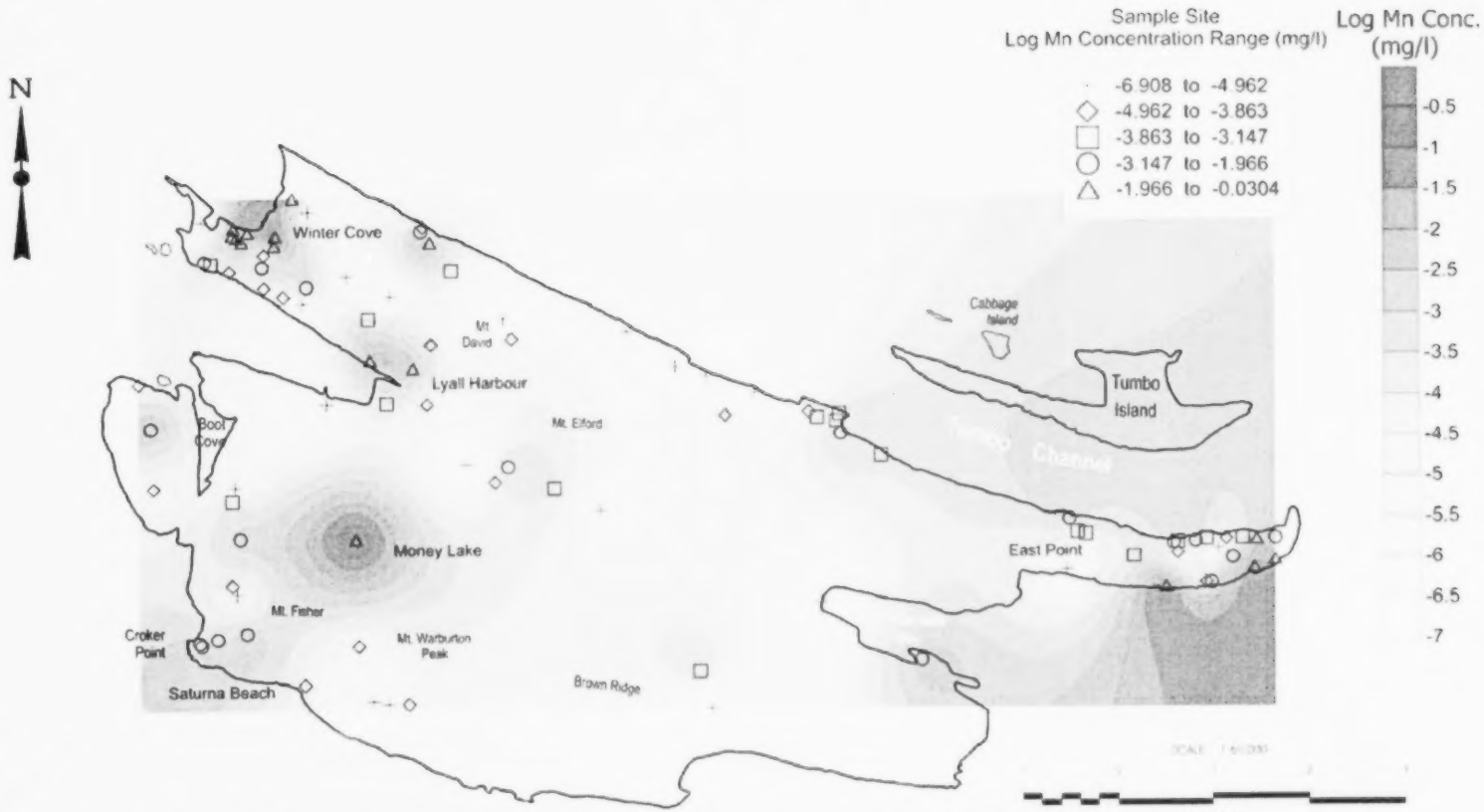


Figure 3a: Contour map showing logarithm of manganese concentrations on Saturna Island

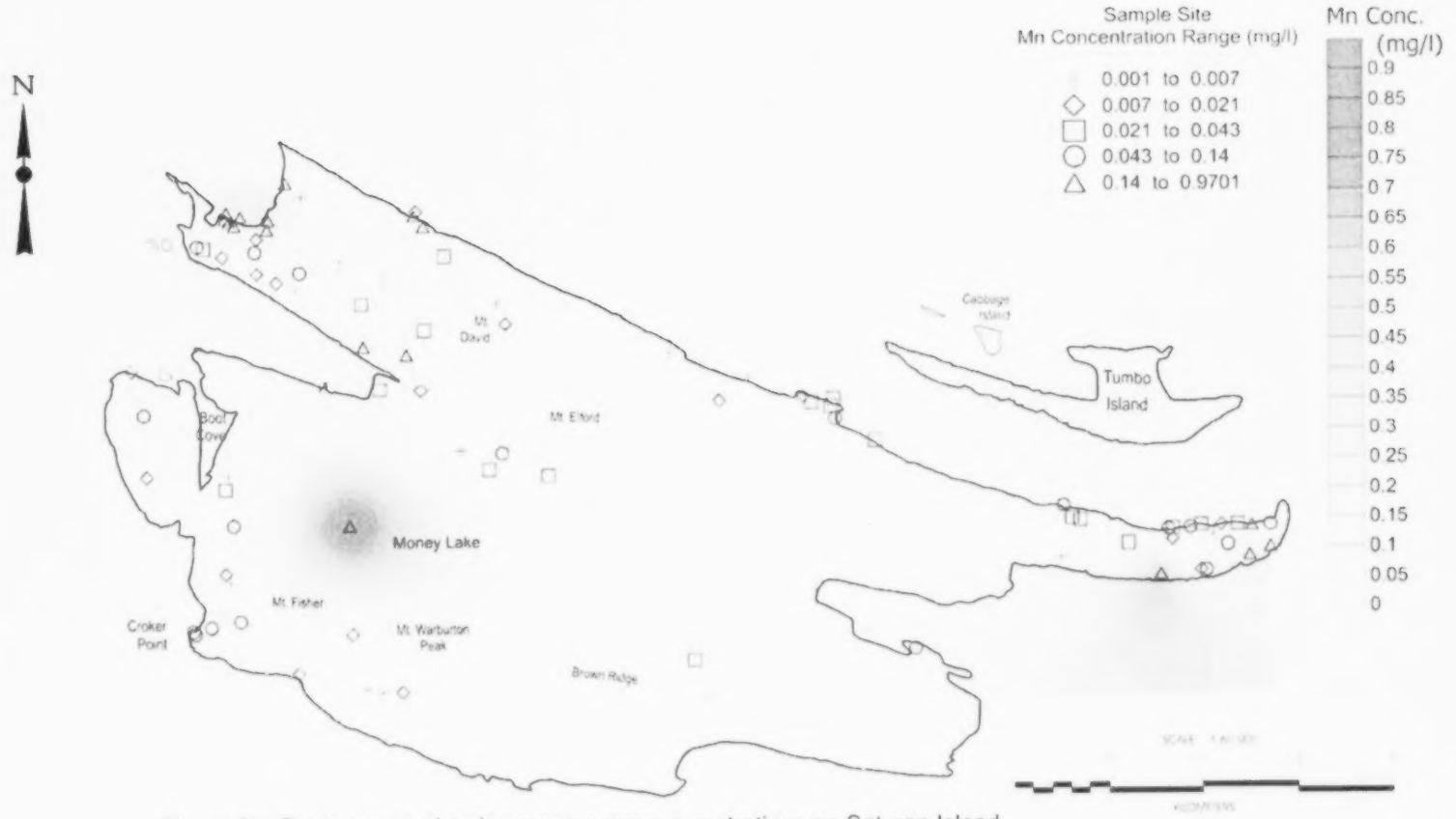


Figure 3b: Contour map showing manganese concentrations on Saturna Island

Figure 4a: Contour map showing logarithm of manganese concentrations on Hornby Island

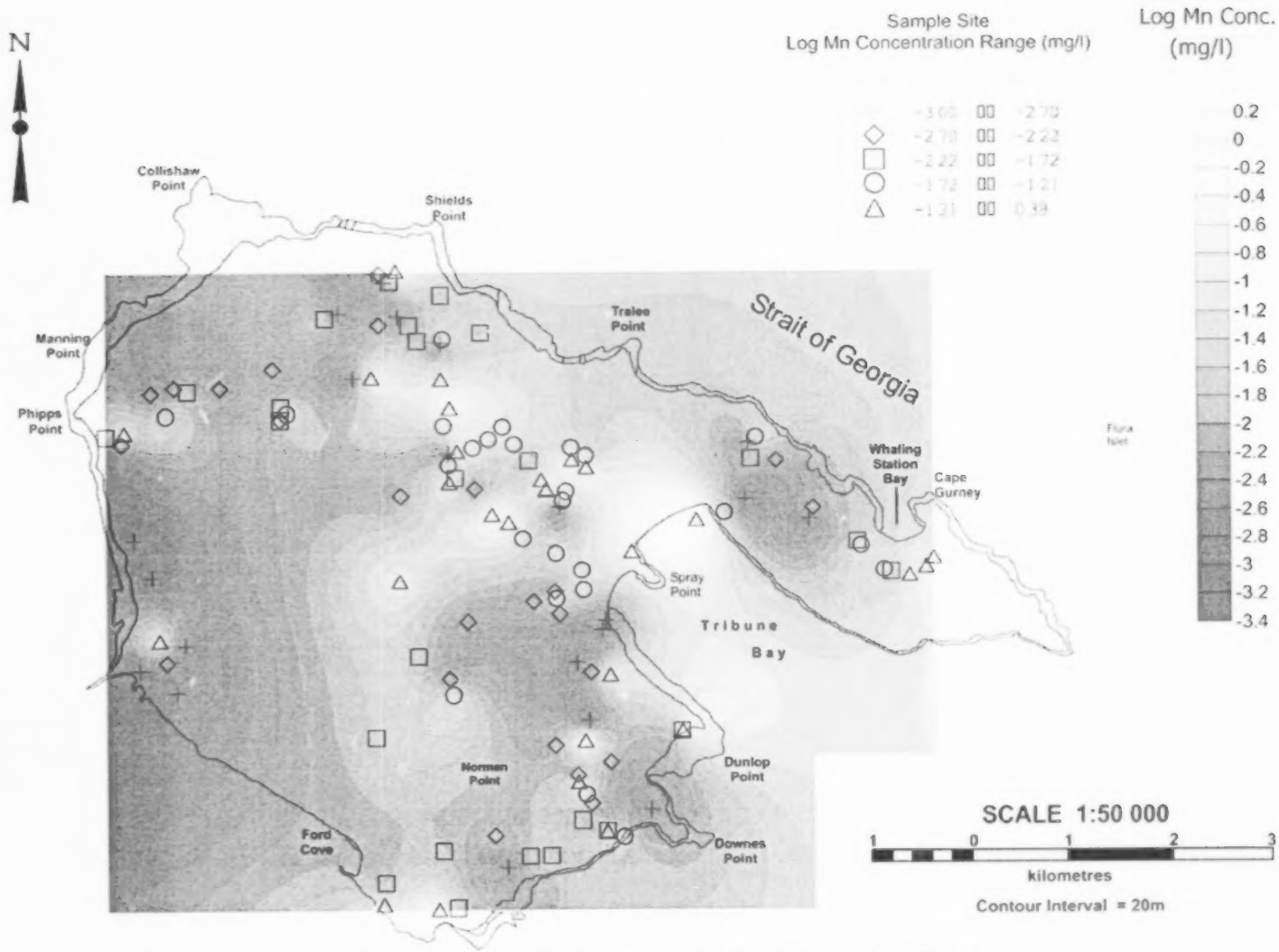


Figure 4a: Contour map showing logarithm of manganese concentrations on Hornby Island

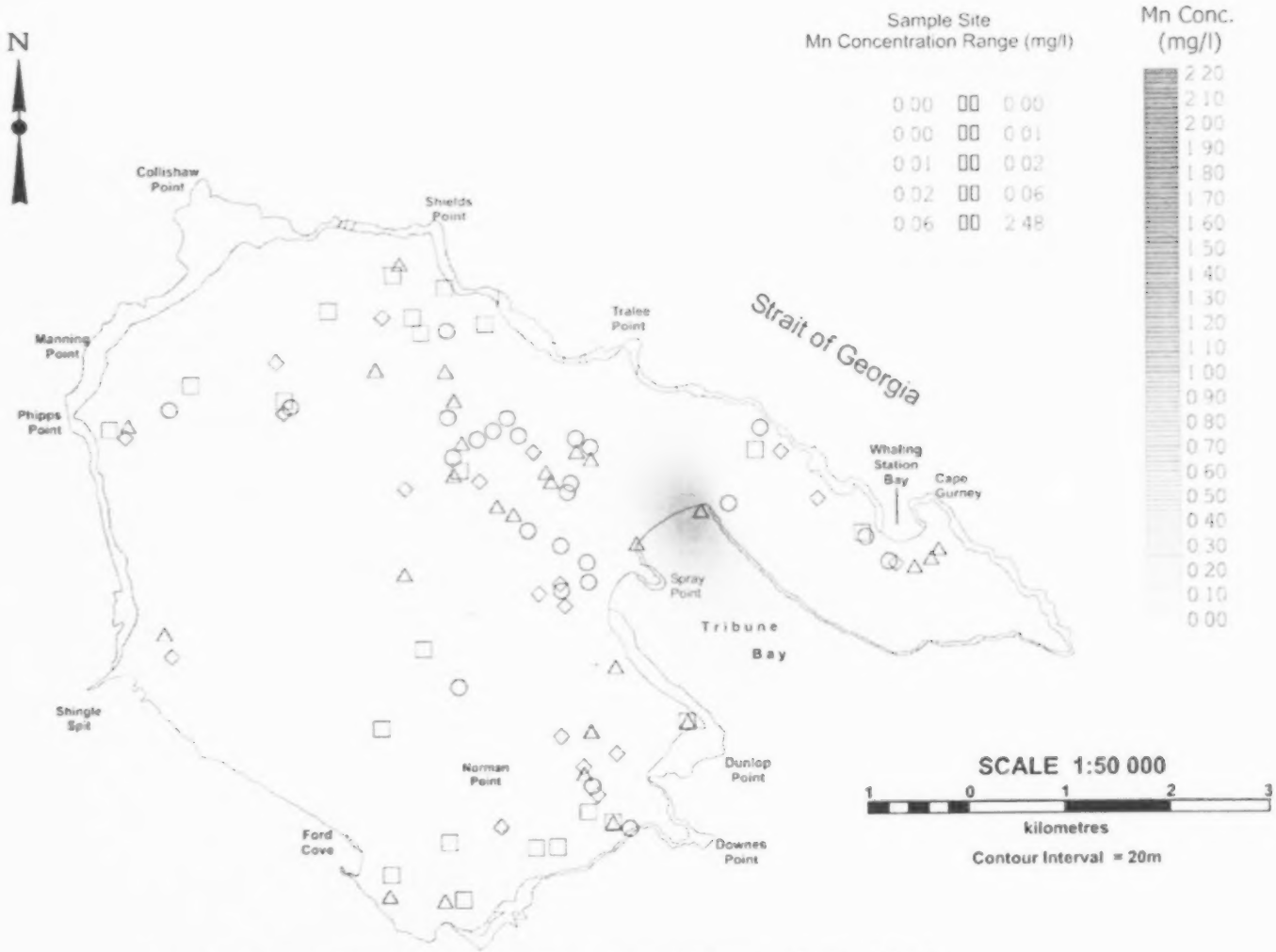


Figure 4b: Contour map showing manganese concentrations on Hornby Island

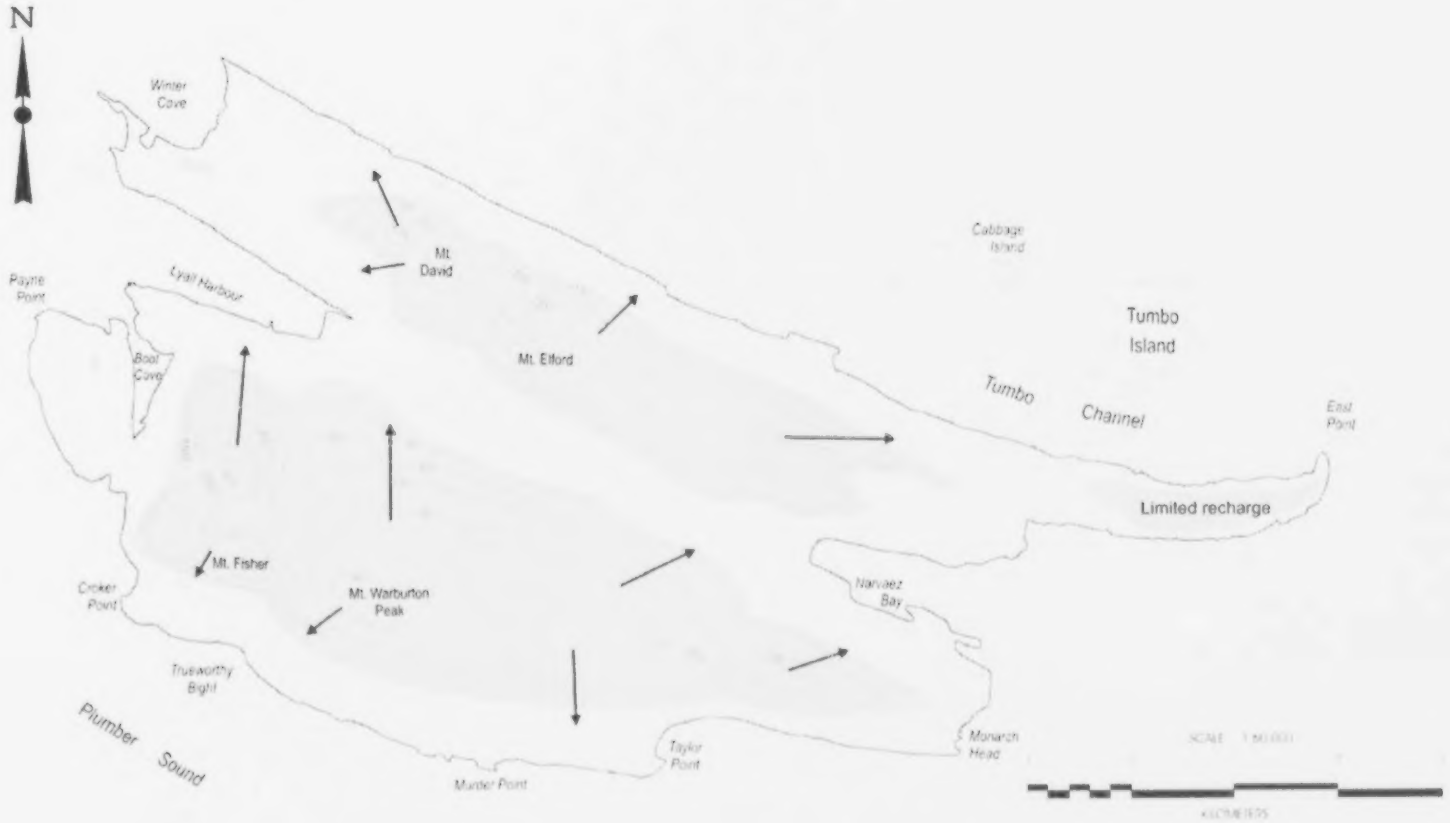


Figure 5: Recharge areas for Saturna Island showing general movement of overland flow and groundwater flow.

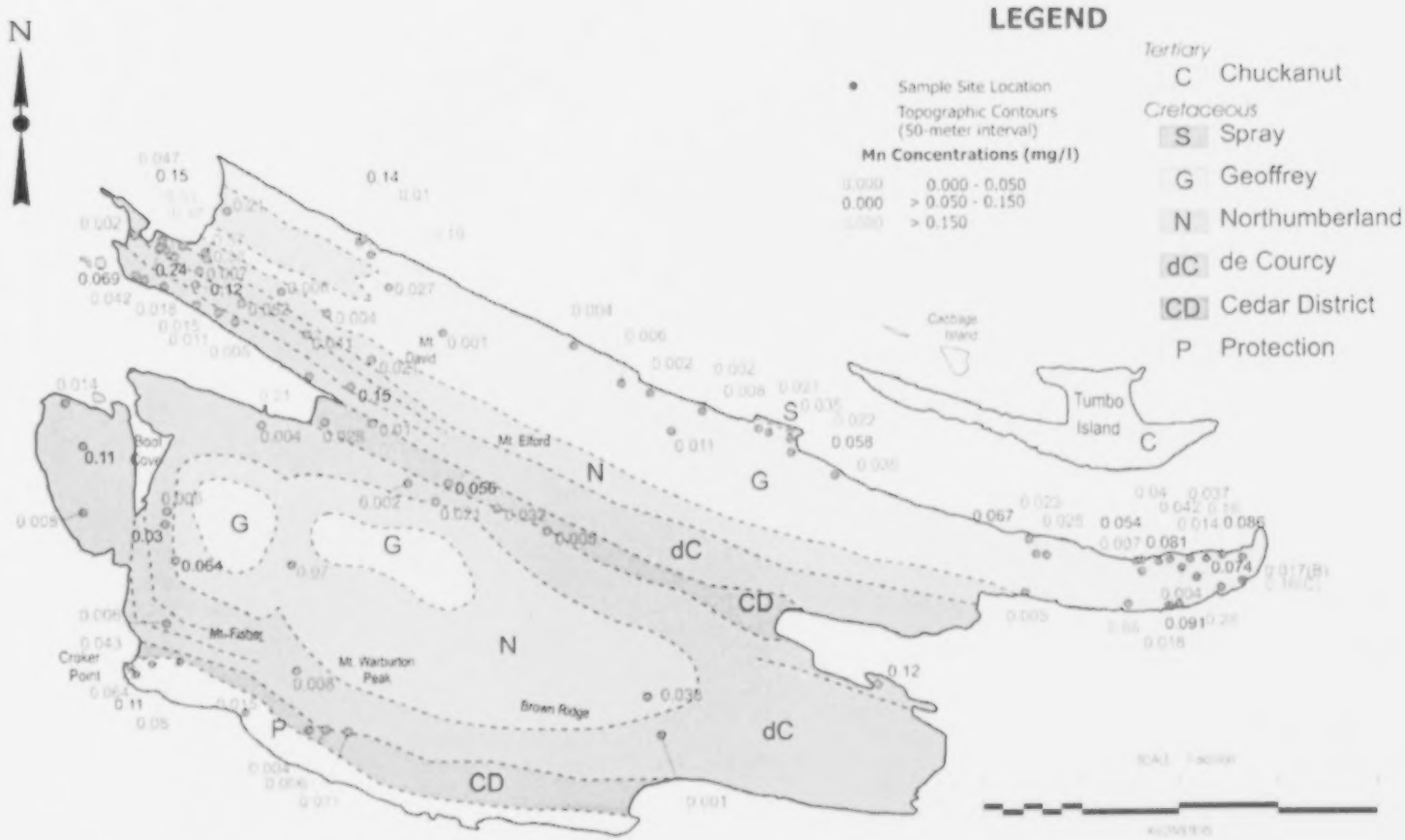


Figure 6: Geology and manganese concentrations for Saturna Island

Figure 5: Recharge areas for Saturna Island showing general movement of overland flow and groundwater flow

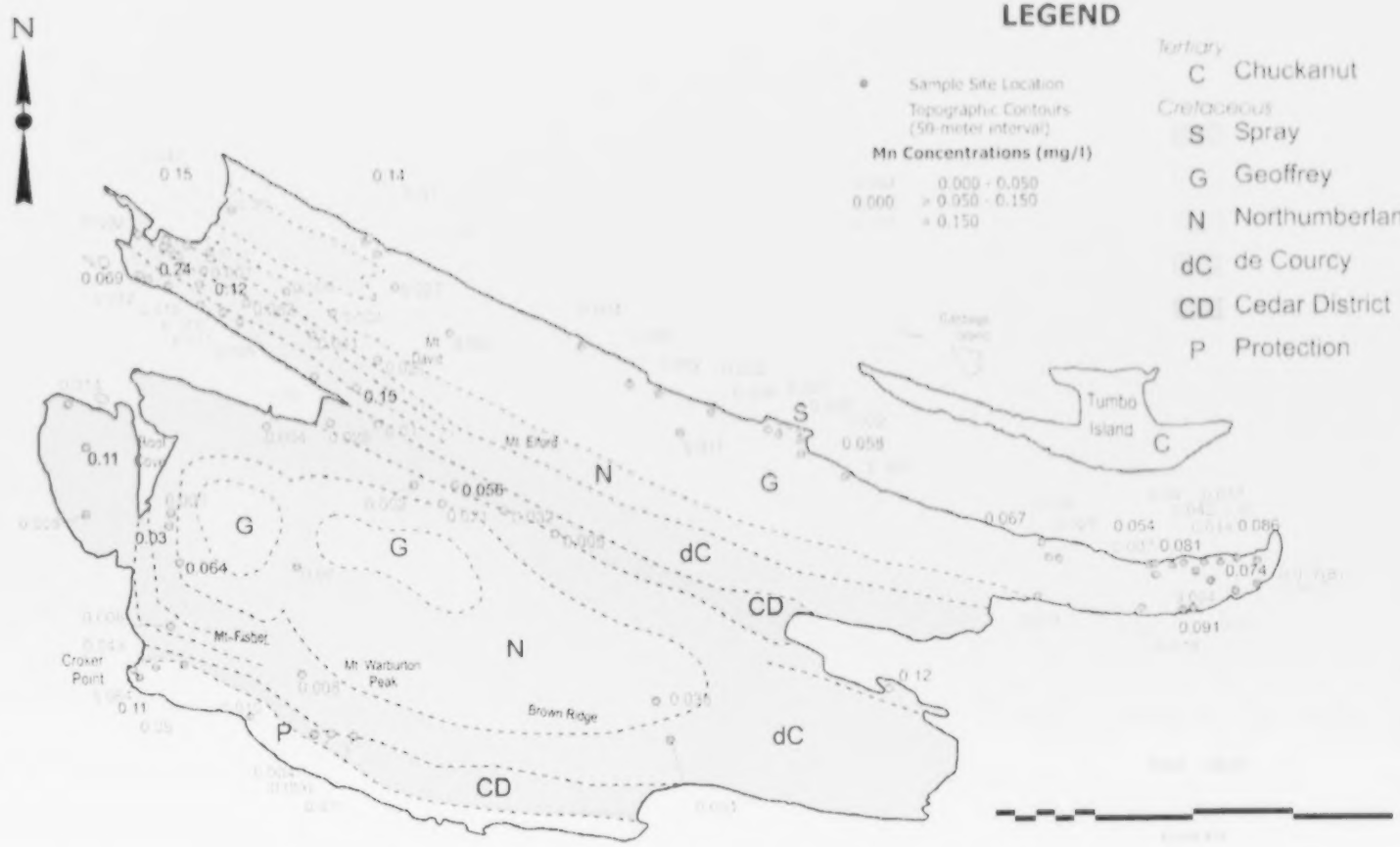


Figure 6: Geology and manganese concentrations for Saturna Island

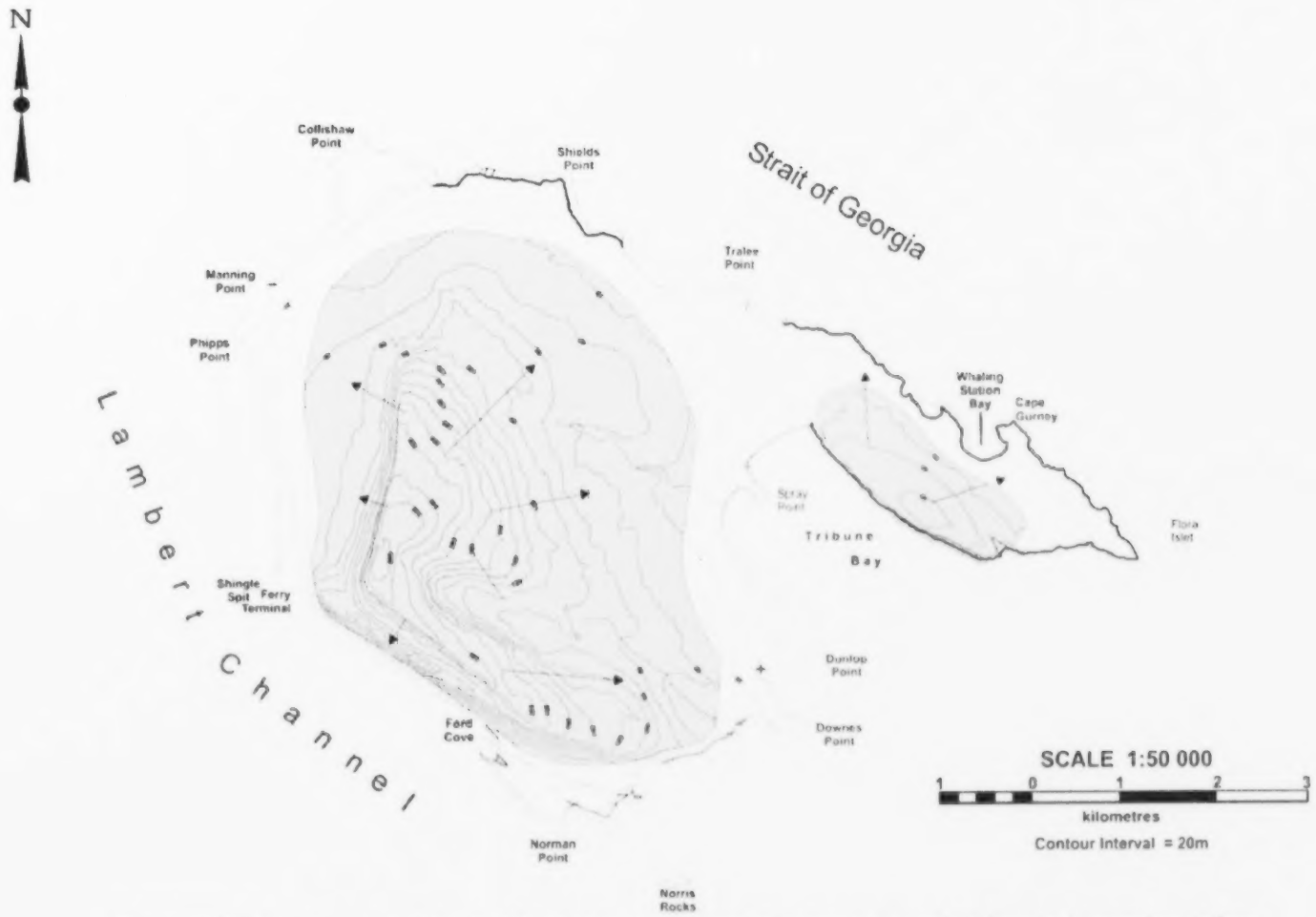


Figure 7: Recharge areas for Hornby Island showing general movement of overland flow and groundwater flow.

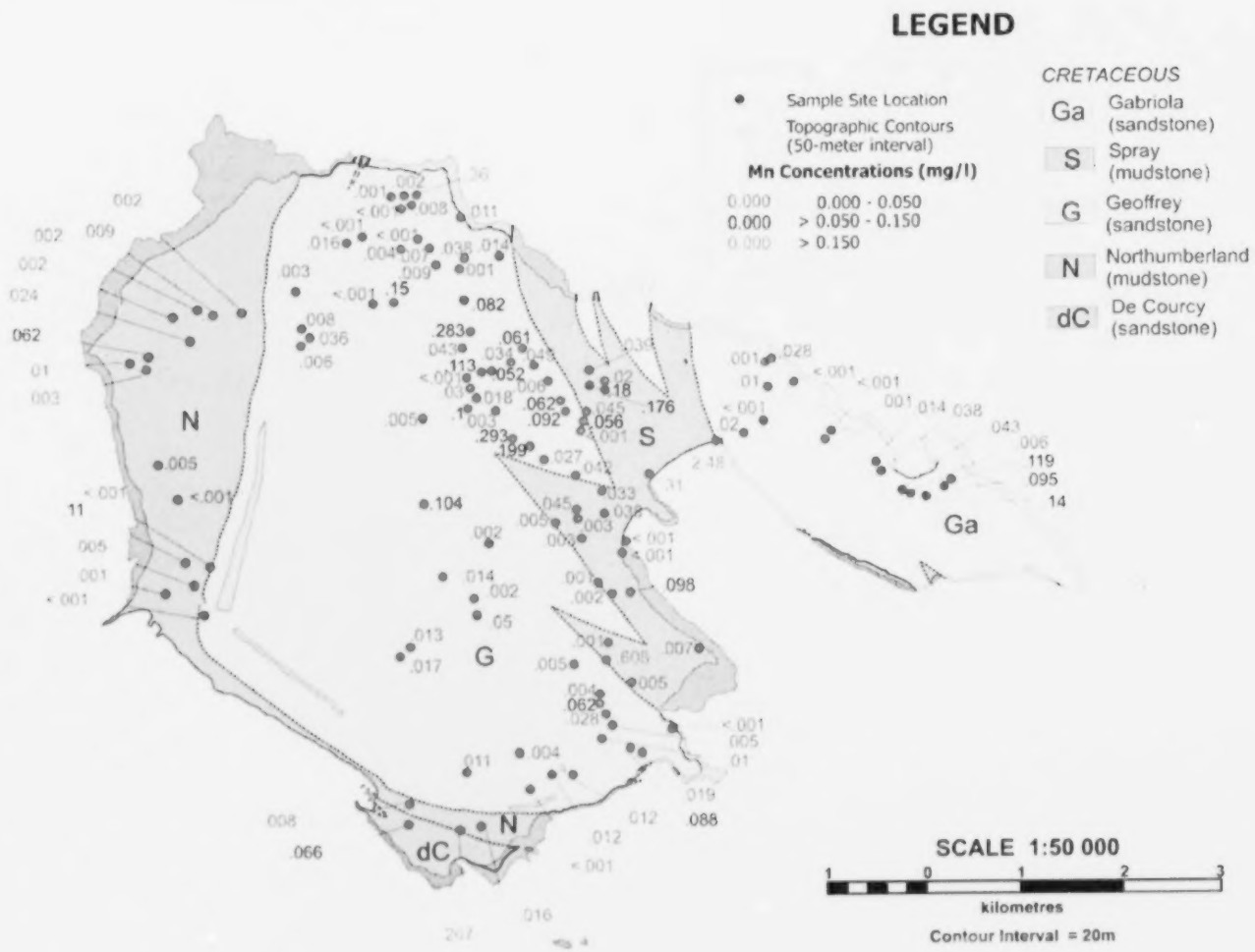


Figure 8: Geology and manganese concentrations for Hornby Island

Figure 7: Recharge areas for Hornby Island showing general movement of overland flow and groundwater flow

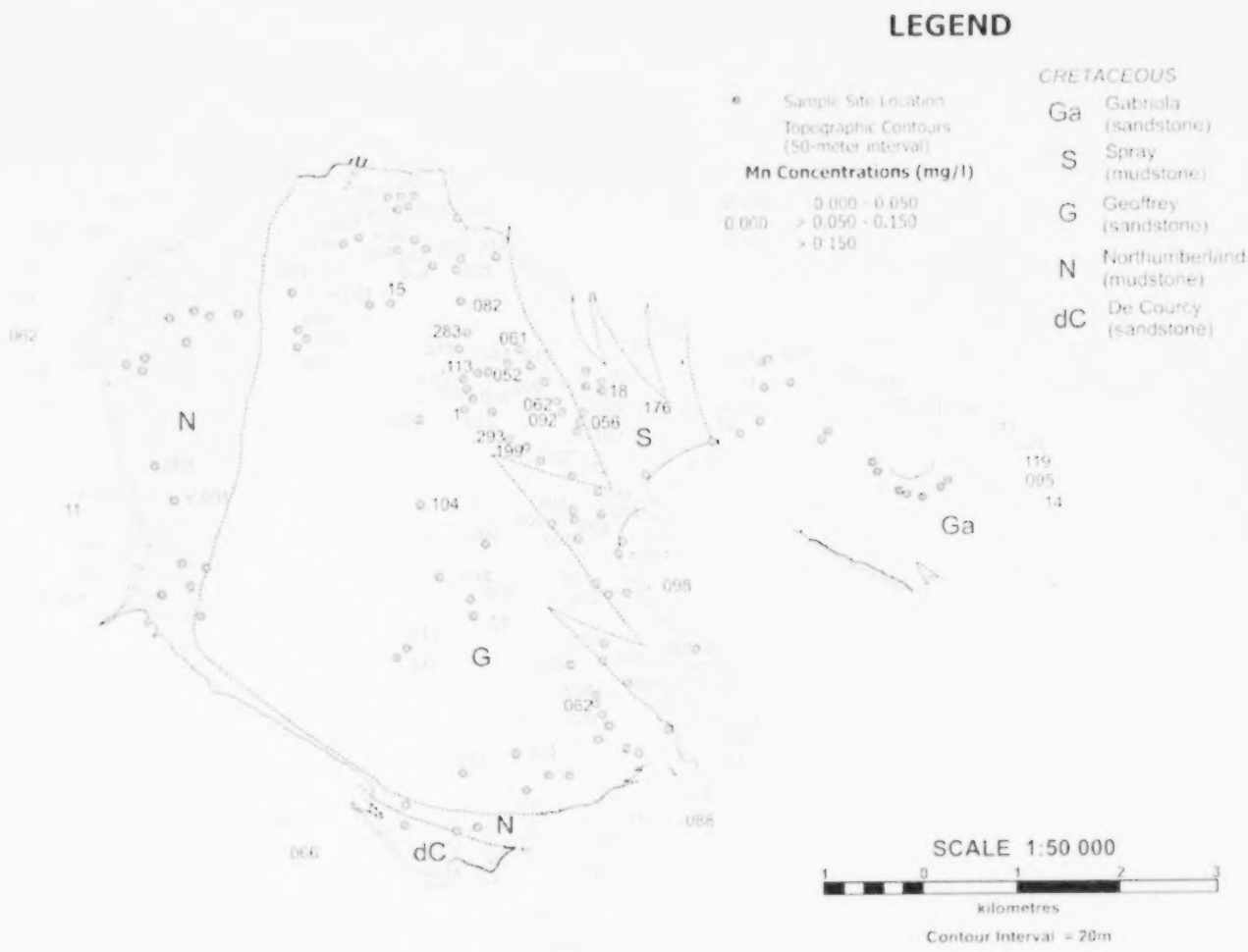


Figure 8: Geology and manganese concentrations for Hornby Island

5 Origin of Manganese

The origin of dissolved manganese in groundwaters has not been the subject of extensive research, and limited information is available on this subject. However, by example, in a study done on the right bank of the Rhone valley, the origin of manganese was considered. At the site, there were excessive concentrations of manganese. In order to identify the origin it was necessary to obtain information about, the geology of the environment; aquifer flow and the physical-chemical conditions of the water and sediments. As well, metal speciation ion sediments and the influence of micro-organisms. With these data researchers were able to determine that the manganese originates from the aquifer, mainly in the form of oxides, which settle on the bed of the river. Manganese release was due to decrease in dissolved oxygen in the groundwater. Under these conditions. Mn(IV) was reduced both chemically and bacterially into Mn (II) soluble form (Vacelet, 1988).

Much of the information required to determine the origin of Mn in the aquifers of the Gulf Islands is already available, and will be considered in future SFU research on the origin of dissolved species in groundwaters on the Gulf Islands. Possible sources are the local sedimentary rocks (mudstones or sandstones or both), or perhaps, saline groundwaters associated with saltwater intrusion or deep saline waters associated with the freshwater/saltwater interface at depth beneath the islands. Under each scenario, there are likely complex chemical reactions (including redox reactions) that serve to ultimately control the concentration of Mn in groundwaters.

Although not a comprehensive study of the origin of dissolved manganese, this section of the report attempts to illustrate the correlation of manganese with other dissolved constituents in groundwater. The methodology employed involved plotting manganese concentrations against the concentrations of other chemical parameters such as anions (e.g., fluoride, chloride, bicarbonate and sulphate), other metals (e.g., barium, boron, calcium, zinc, iron, magnesium, sodium and strontium) and other chemical parameters (including pH and cation molar ratio). Cation molar ratio (or CMR) is defined as the ratio of sodium over the sum of calcium and magnesium. This parameter is a quick indicator of the presence of cation exchange. When the CMR is significantly higher than one, this indicates an excess of sodium beyond that which can be accounted for by cation exchange with calcium and/or magnesium. The correlation of dissolved manganese with depth of well was only done only for Saturna Island, and no correlation was found.

It was unfortunate that dissolved oxygen values were not available in the data set, as it would have been interesting to see if the high manganese levels are associated with anaerobic conditions. Future studies will incorporate dissolved oxygen. Also, information on the speciation of the manganese present in the well could have been used to see if there was a correlation between higher oxide forms of manganese with an increase in pH. This could be looked at in further studies.

5.1 Saturna Island

Positive correlations were observed between dissolved manganese and sulphate (SO_4) and chloride (Cl) (Figure 9a), although the trend is only slightly positive and there is a large scatter in the data as evidenced by the small R^2 values. Of the metals, a positive correlation was observed between manganese and most metals tested including iron (Fe), strontium (Sr), barium (Ba), magnesium (Mg), calcium (Ca), sodium (Na) and strontium (Sr) (Figures 9b and c). In all cases there was a large degree of scatter. No correlation was observed between manganese and either boron (B) or zinc (Zn). No correlation was observed between manganese and either pH or CMR (Figure 9d).

5.2 Hornby Island

Positive correlations were observed between dissolved manganese and possibly chloride although the trend is very poor (Figure 10a). Both fluoride (F) and bicarbonate (HCO_3) observed negative correlations. In contrast to Saturna data, sulphate showed no correlation. Of the metals, positive correlations were observed between iron, barium, magnesium, calcium, and strontium. A poor negative correlation was observed with sodium and boron. No correlation was observed between magnesium and either pH or CMR.

5.3 Discussion

Although not entirely conclusive because of the poor positive or negative correlations observed between many of the species tested and manganese, it appears that manganese concentrations are related, albeit perhaps moderately, to other dissolved species. It is not surprising that manganese and iron show a relatively strong correlation, as these two species are commonly found together in waters. The slight positive correlation with barium, calcium, magnesium and strontium, and the lack of a strong correlation with either sodium or chloride suggest limited association with seawater, although this explanation has not been ruled out entirely. The dynamic geological history of the Gulf Islands, which includes submergence during the Pleistocene and re-emergence at the end of that period, has likely contributed to a complex geochemical evolution of groundwaters. Nevertheless, it is likely that manganese exists in the local geology of both islands, and is contributed to the groundwater as a result of normal dissolution processes. The elevated concentrations of manganese found in some areas is likely the result of superimposed chemical processes, such as redox, that act to control the amount of dissolution that takes place.

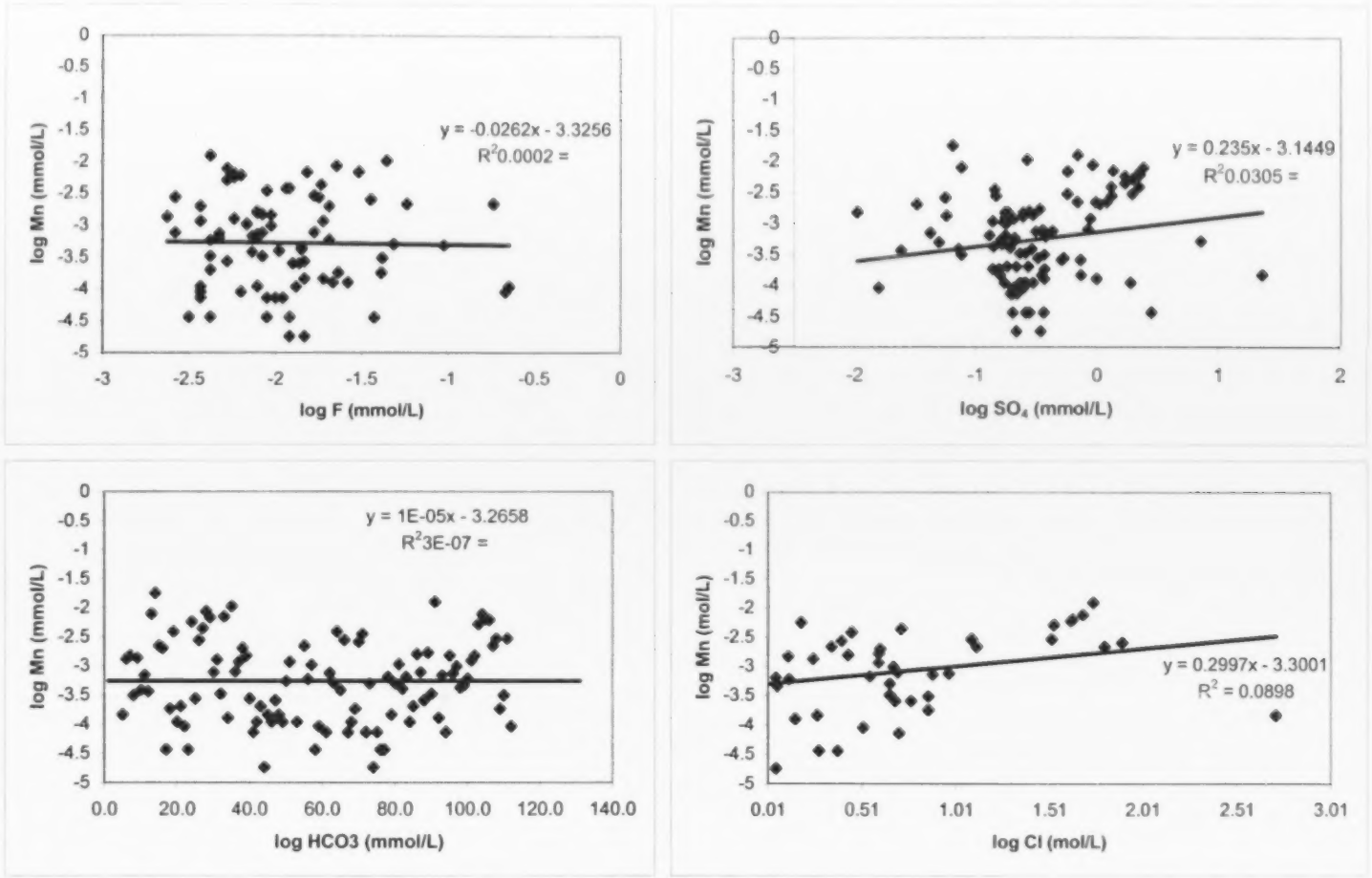


Figure 9a: Correlation graphs between manganese and anions on Saturna Island

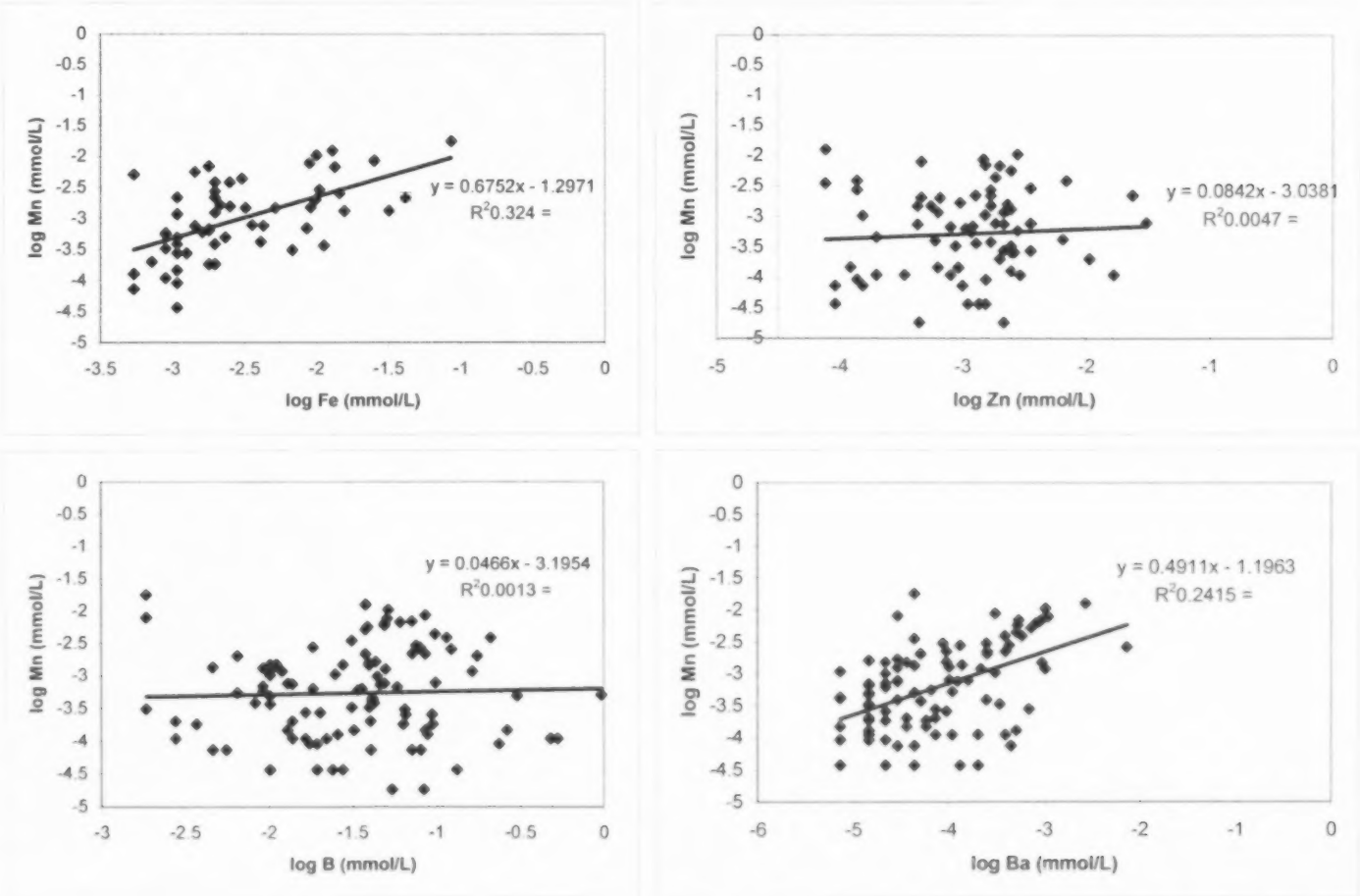


Figure 9b: Correlation graphs between manganese and metals on Saturna Island

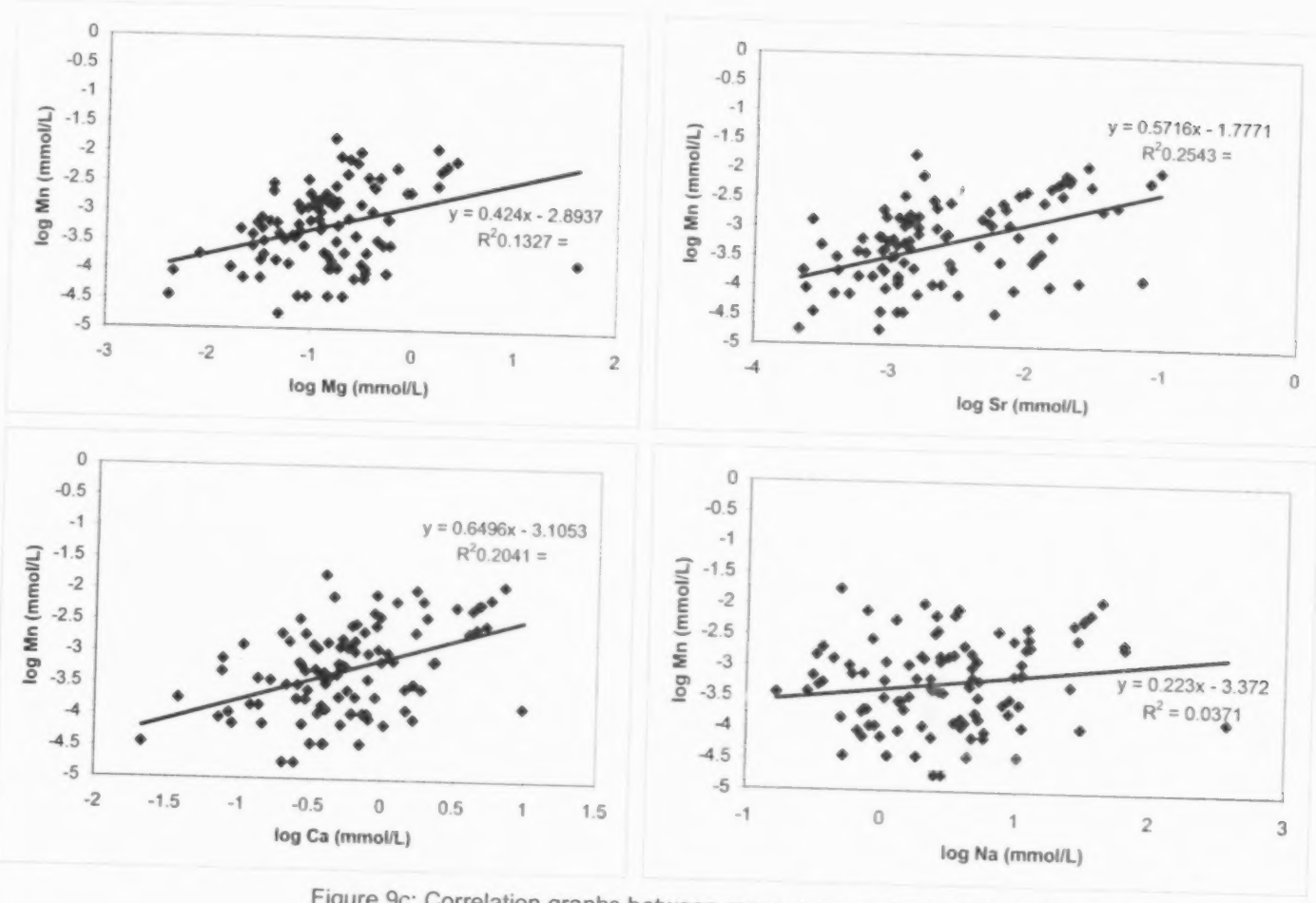
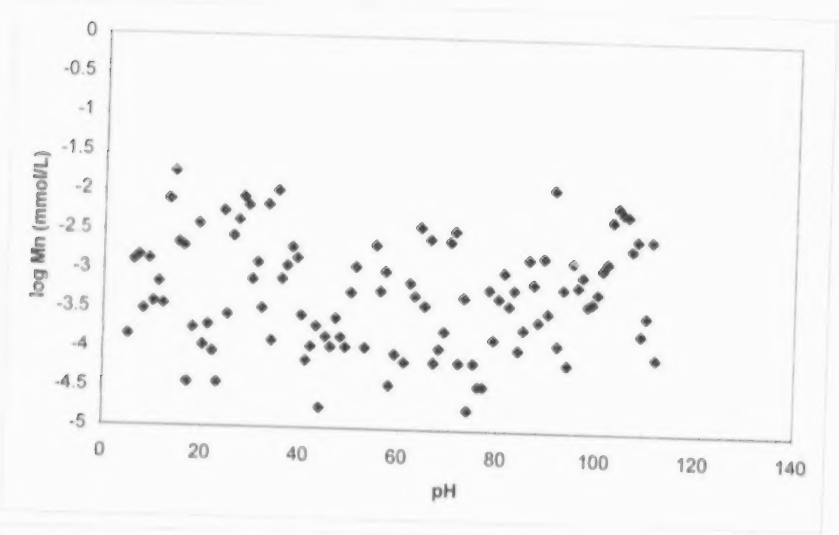


Figure 9c: Correlation graphs between manganese and metals on Saturna Island



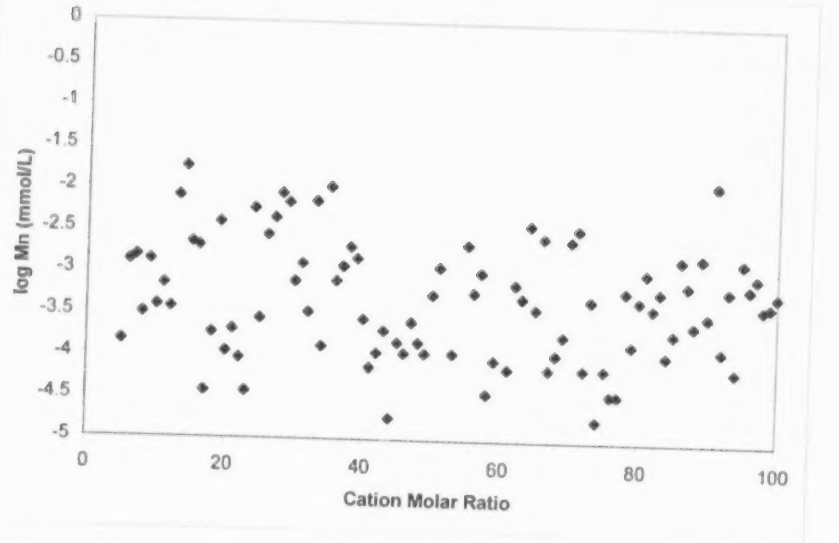
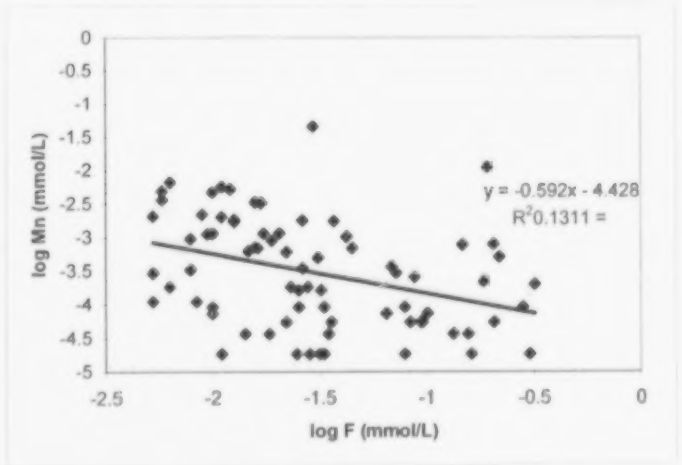
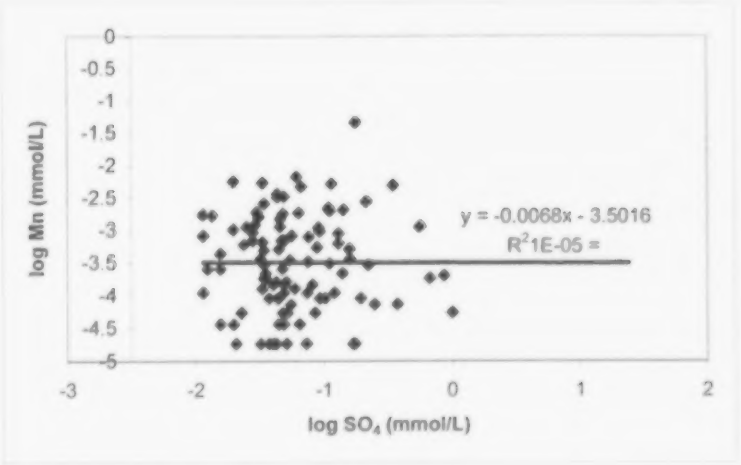
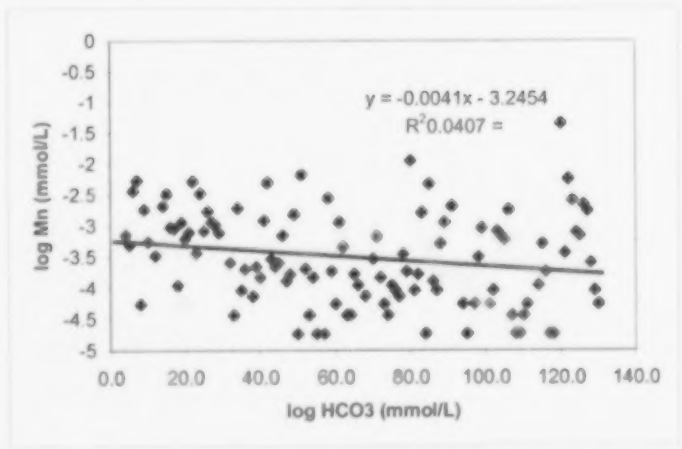


Figure 9d: Correlation graphs between manganese and pH and CMR on Saturna Island







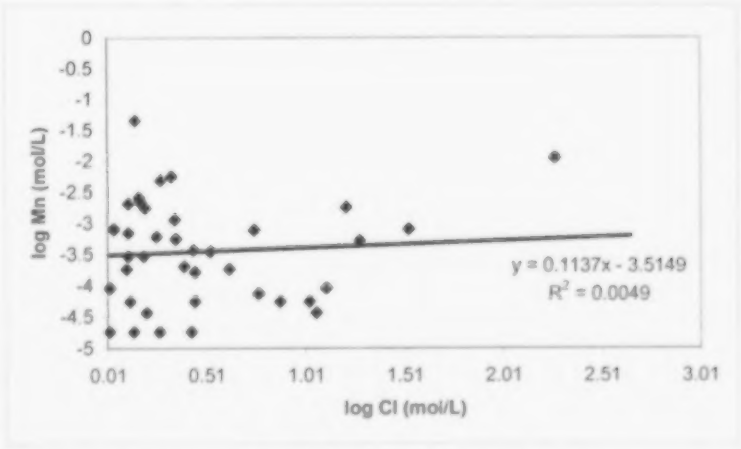


Figure 10a: Correlation graphs between manganese and anions on Hornby Island

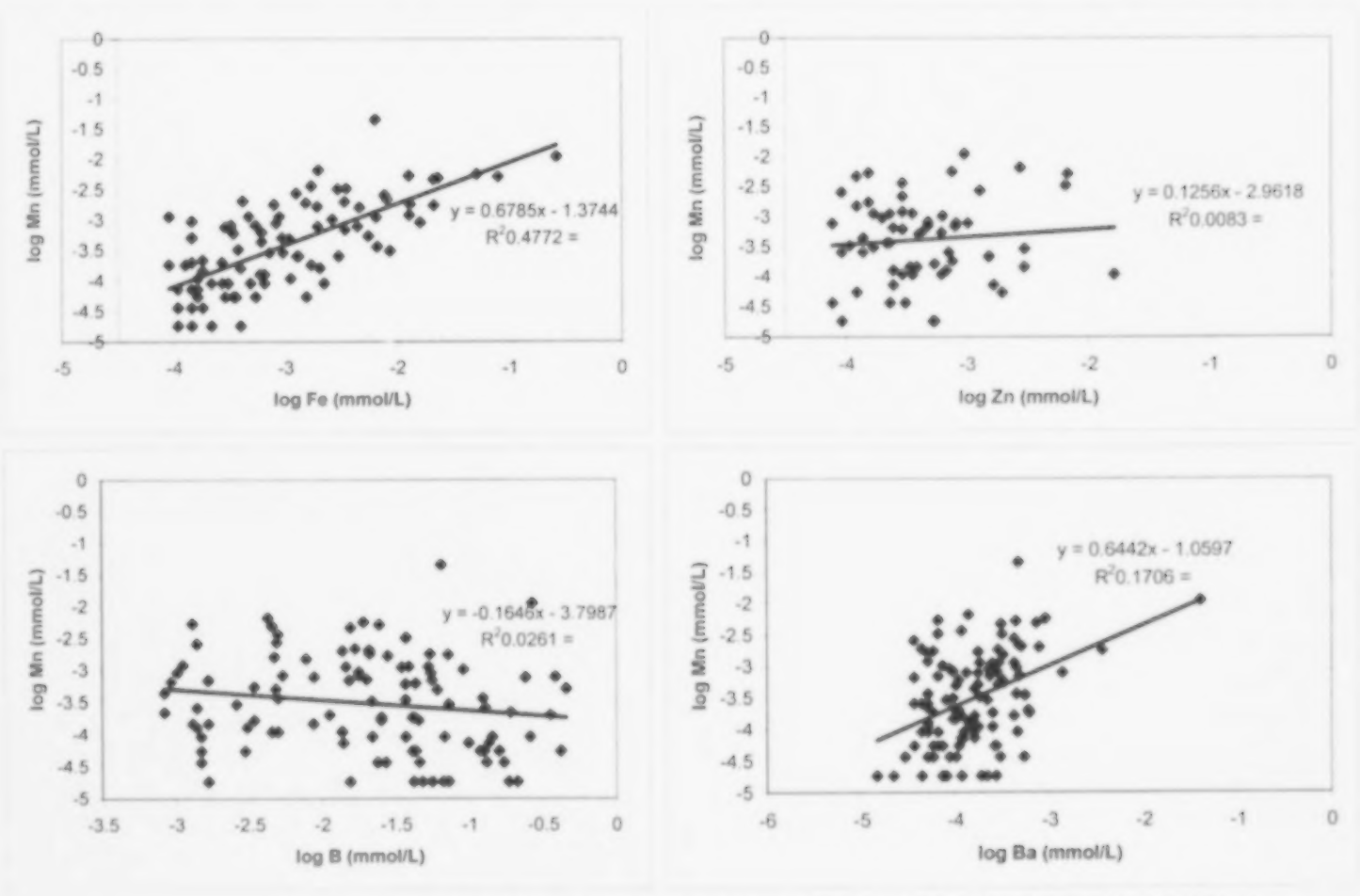


Figure 10b: Correlation graphs between manganese and metals on Hornby Island

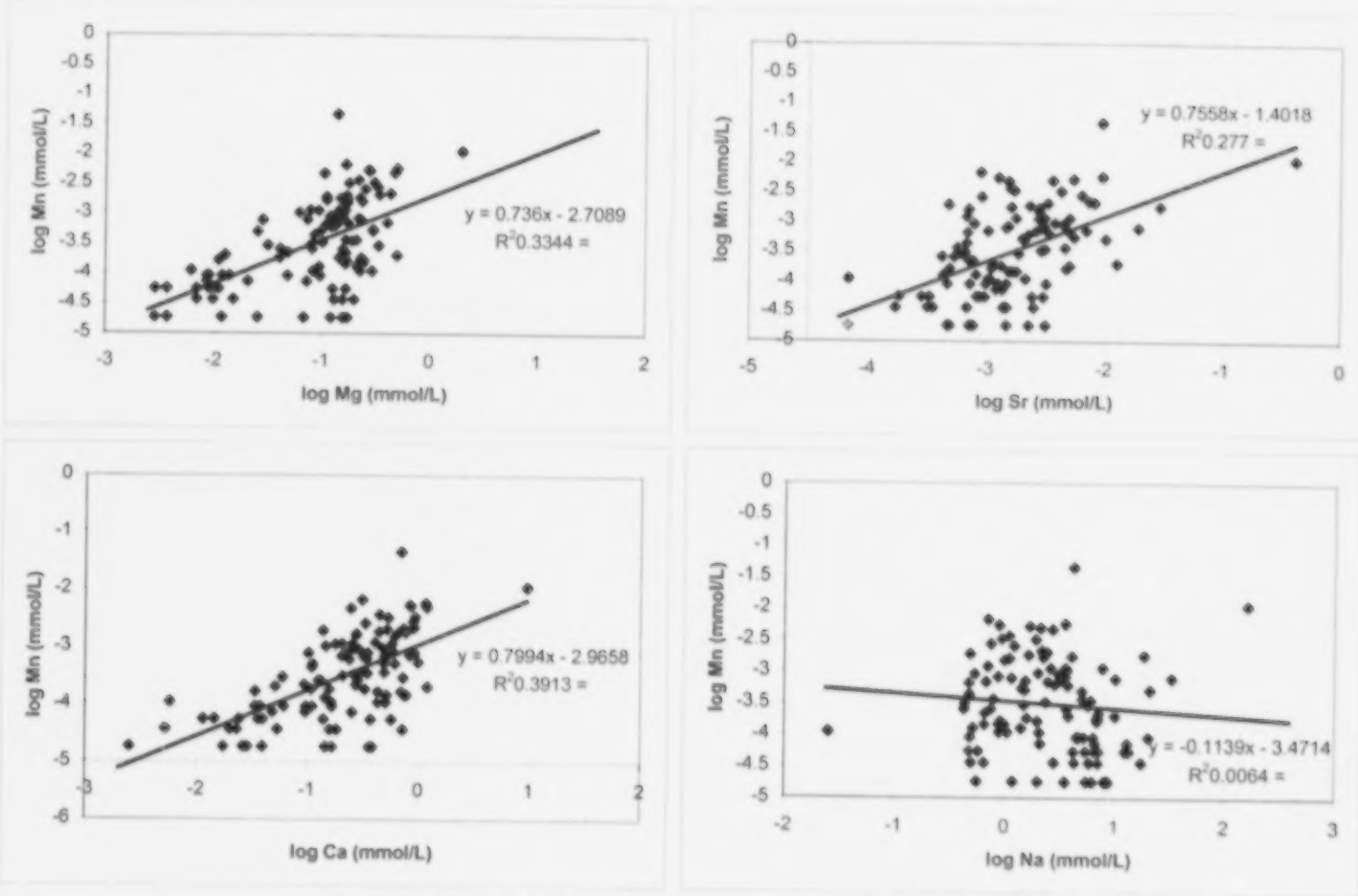
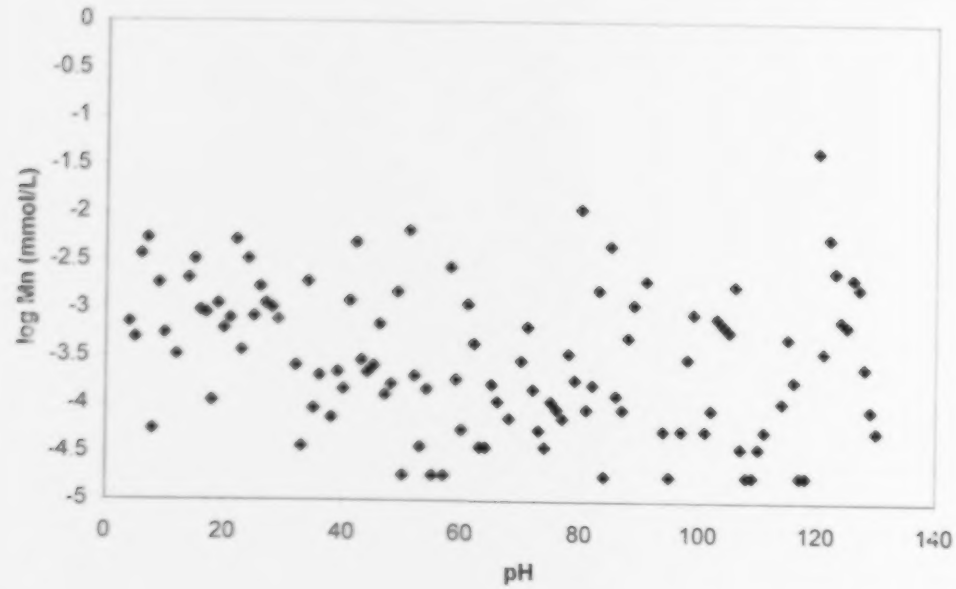


Figure 10c: Correlation graphs between manganese and metals on Hornby Island



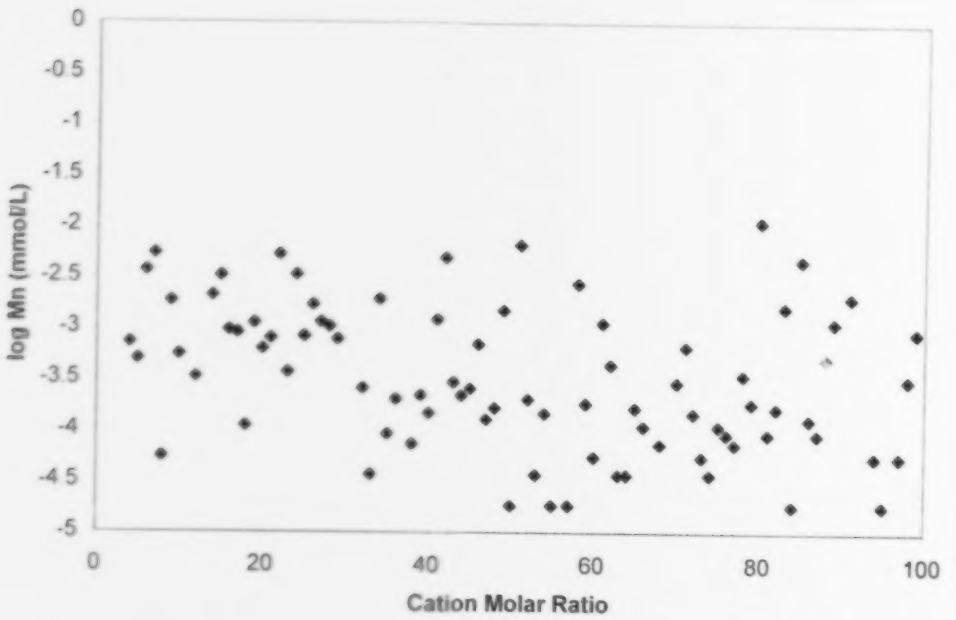


Figure 10d: Correlation graphs between manganese and pH and CMR on Hornby Island

6 Conclusions

For both aesthetic and economic reasons, the maximum admissible concentrations of iron and manganese have been limited to 0.05 mg/L. Common to both Saturna and Hornby Island are the relationships between manganese and iron, calcium, strontium and barium. It is interesting to note with respect to human health that the absorption of manganese is decreased with the increased availability of calcium, magnesium and iron. It is very difficult to determine the effects of manganese in humans due to so many other factors involved in adsorption. In addition, determining the source and daily intake of the manganese can be very difficult because manganese is in the air, water, soil and the food we eat.

There is some controversy as to whether neurological effects exhibited with inhalation exposures will also occur with oral exposures. It is not certain that manganese ingested in large amounts will have the same effect as the inhalation of manganese dust. To date there have been few studies done on this subject and no convincing evidence of toxicity in humans associated with the consumption of manganese in drinking water.

References

Aschner, M. 2000. Manganese: Brain Transport and Emerging Research Needs. Environmental Health Perspectives Supplements, 108(3), pp. 429–433.

ASTDR. 1992. Toxicological Profile for Manganese. http://astdr1.astdr.cdc.gov.

Federal-Provincial Subcommittee on Drinking Water. 1999. Guidelines for Canadian Drinking Water Quality: Supporting Documents and Summary of Guidelines for Canadian Drinking Water Quality: Health Canada.

Finely, J. and Davis, C. 1999. Manganese Deficiency and Toxicity: Are High or Low Dietary Amounts of Manganese Cause for Concern? Biofactors, 10(1), p158.

Klaassen, C.D. 1986. Casarett and Doull's Toxicology. Macmillan Publishing, New York.

Klimis-Tavantzis, D. 1994. Manganese in Health and Disease. CRC Press Inc., London.

Kondakis, L. 1989. Possible Health Effects of High Manganese Concentration in Drinking Water. Archives of Environmental Health, 44(3), pp. 175-178.

Matsuo, G.P. 2000. Chemical Evolution of Groundwater on Hornby Island, B.C. Unpublished B.Sc. Honours thesis, Department of Earth Sciences, Simon Fraser University, Burnaby, B.C. 102 pp.

Suchy, M. 1998. Physiographic and Geologic Controls on Groundwater Salinity Variations on Saturna Island, B.C. Unpublished B.Sc. thesis, Department of Geography, Simon Fraser University, Burnaby, B.C.

Vacelet, E. 1990. Groundwater Pollution By Manganese. Manganese Speciation: Application to the Selection and Discussion of an In situ Groundwater Treatment. The Science of the Total Environment, 84 (1989), pp. 169-183.

Varner, D. 1996. Drinking Water: Iron and Manganese Web Guide. http: www.ianr.unl.edu/pubs/water/g1280.htm.

Vierregge, P. 1995. Long Term Exposure to Manganese in Rural Well Water Has No Neurological Effects. The Canadian Journal of Neurological Sciences, 22, pp. 286-289.

Water Management Branch, Ministry of Environment and Resource Division, Ministry of Environment, Lands and Parks. 2001. Ambient Water Quality Guidelines for Manganese: Overview Report. National Library of Canada Cataloguing in Publication Data.

World Health Organization. 1996. Guidelines for Drinking-Water Quality, 2nd ed, vol. 2. Health Criteria and Other Supporting Documents pp. 50-51 and pp. 276-284.

Zumdahl, S. 1995. Chemical Principals. D.C. Heath Company, Toronto.